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The virial coefficients of a system of nonpolar molecules of arbitrary symmetry

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The dielectric second virial coefficient, pressure second and third virial coefficients of a gas of nonspherical molecules of arbitrary symmetry have been calculated for a set of force parameters which has been found suitable to explain the dilute gas viscosity data. The influence of a large number of orientation dependent pair—and three-body nonadditive interactions have been taken into account. The relative contribution of each branch of pair and triplet interactions has been evaluated as a function of temperature. The theoretical results have been compared with the experimental data of N_2, CO_2 and C_2H_4. The agreement between theory and experiment is satisfactory for all the systems. The quadrupole moments and shape parameters obtained are reasonable.

1. Introduction

Valuable information about anisotropic interactions can be derived from the study of virial coefficients of the equation of state. In recent years, therefore, considerable attention has been paid to evaluate the contributions of the nonsphorical interactions to the virial coefficients of polyatomic gases. The extent to which the shape of molecules contribute to the transport and pressure second virial coefficients of nonpolar molecules have been studied on a 12-12-6 potential model in a previous paper (Das Gupta *et al* 1973) (which we refer to as I). In this paper the effects of this term on the dielectric second and pressure third virial coefficients of nonpolar molecules have been studied. In particular, an attempt has been made to show that the transport and virial coefficients of a system of nonpolar molecules can be explained with the same set of force parameters, if molecular asymmetry is explicitly taken into account in the calculation of virial coefficients.

The potential energy of interaction of a pair of molecules has the forms

$$U(1, 2) = \phi_{12}(r_{12}) + V_{12}(r_{12}, \omega_1, \omega_2), \qquad \ldots \quad (1)$$

where ω_i represents the Euler angles θ_i, ϕ_i and ψ_i specifying the orientation of molecule i; ϕ_{12} is the central potential between the molecules 1 and 2 and V_{12}, arising from tensor forces, contains all the angle dependence of pair interaction. For this interaction we write

$$V_{ij} = V_{ij}^{perm} + V_{ij}^{in} + V_{ij}^{dis} + V_{ij}^{sh} \qquad \ldots \quad (2)$$

where V_{ij}^{perm} is the interaction between permanent multipole moments of the molecules, V_{ij}^{in} the interaction of induced multipole moments in one molecule with the permanent moments in the other molecule, V_{ij}^{dis} the interaction between anisotropic dispersion forces of the molecules, and V_{ij}^{sh} the angle-dependent overlap interaction.

For three-body potential, we write

$$U(1, 2, 3) = \sum_{j>i=1}^{3} U(i, j) + V(1, 2, 3) \quad \ldots (3)$$

where $V(1, 2, 3)$ is the three-body nonadditive interaction. This interaction arises from two sources : (i) from the dispersion and short-range three-body exchange forces, and (ii) from classical electric induction interactions between asymmetric molecules. Thus

$$V(i, j, k) = V_{ijk}^{in} + V_{ijk}^{dis} + V_{ijk}^{rep} \quad \ldots (4)$$

For the calculation we take the functional form of these interactions as summarized by Stogryn (1969, 1970).

The dielectric second virial coefficient is known to be more sensitive to the asymmetric interactions than the second virial coefficient and thus may be useful in testing potential parameters found suitable for the representation of viscosity and second virial coefficient data (Das Gupta *et al* 1973). The calculation of dielectric second virial coefficient has been presented in the following section using the method of Buckingham & Pople (1955). The present calculation of dielectric second virial coefficient includes more terms for nonspherical interactions than hitherto included. The series expansion has been carried out to sufficient length so that the proper convergence is achieved to a sufficient degree of accuracy.

The pressure third virial coefficient $C(T)$ which involves the simultaneous interaction of three molecules is of considerable importance. First because it is relatively more sensitive to the potential curve and thus allows a severe test of an assumed model and secondly it gives valuable informations regarding the role of three-body nonadditive interactions, at higher densities (Singh & Singh 1972, 1974).

The third virial coefficient of a gas of nonspherical molecules has been calculated by many workers assuming the pairwise additivity of the potential. Three-body nonadditivity of the potential was neglected. The nonadditive interactions and its influence on the third virial coefficient was studied in detail by Sherwood & Prausnitz (1964), Graben *et al* (1966) and Sherwood *et al* (1966) for spherically symmetric molecules and by us (Singh & Singh 1971, 1972, 1974) for polar molecules. For the mixture of nonspherical molecules of arbitrary

symmetry Stogryn (1969, 1970) has studied the influence of a large number of angle-dependent pair- and three-body nonadditive interactions on the third virial coefficient. Stogryn's study includes electrostatic, induction and anisotropic dispersion pair interactions and three-body nonadditive interactions arising from the induction and dispersion forces. In the present paper we consider all branches of pair and triplet interactions discussed above and represent the viscosity, dielectric second virial coefficient, pressure second and third virial coefficients with the same set of force parameters. Theoretical results are compared with the experimental data of three nonpolar polyatomic gases (N_2, CO_2 and C_2H_4).

2. Calculation and Results

(a) *Dielectric second virial coefficient*

The dielectric second virial coefficient which measures the deviation from Clausius-Mossotti formula owing to two-body interaction can be written as (Buckingham & Pople 1955)

$$B_\varepsilon(T) = B_{\varepsilon(in)} + B_{\varepsilon(or)}. \qquad \ldots (5)$$

The first term results from the interaction of dipole moments induced by the external field and the second term due to orientational forces. The expressions for $B_{\varepsilon(in)}$ and $B_{\varepsilon(or)}$ are

$$B_{\varepsilon(in)} = \frac{4\pi N^2}{3\Omega} \int \left[\tfrac{1}{2} \left(\partial \frac{(m_1+m_2)}{\partial E_0} \right) \cdot e - \alpha \right] \exp[-U(1,2)/kT] d\tau \qquad \ldots (6)$$

$$B_{\varepsilon(or)} = \frac{4\pi N^2}{9kT\Omega} \int \tfrac{1}{2}(m_1+m_2)^2 \exp[-U(1,2)/kT] d\tau. \qquad \ldots (7)$$

Here e is the unit vector along the external field E_0, α the mean polarizability, and m_1 and m_2 are the induced moments and only the contributions independent of E_0 are to be evaluated to obtain the low field polarization. The integral is over all relative configurations of the pair in the spherical volume V, $d\tau = \Omega V$, where Ω is the integral overall orientational coordinates.

The induced moments in the first approximation are represented by the polarizability $\bar{\alpha}$ in the fields E_1 and E_2 of external charges and the multipole moments. The resultant values of m_1 and m_2 from these fields and the dipole field of the induced moment of the other molecule satisfy the equations

$$m_1 = \bar{\alpha} E_1 + \frac{\bar{\alpha}}{r^3} [3(m_2 . e_{12}) e_{12} - m_2]$$

$$m_2 = \bar{\alpha} E_2 + \frac{\bar{\alpha}}{r^3} [3(m_1 . e_{12}) e_{12} - m_1]$$

where e_{12} is a unit vector along the intermolecular separation r.

The series expansion in powers of α/r^3 *yields*

$$m_1 = \alpha E_1 + \frac{\alpha^2}{r^3}[3(E_2.e_{12})e_{12}-E_2]+\frac{\alpha^3}{r^6}[3(E_1.e_{12})e_{12}+E_1]+\ldots \quad \ldots (8)$$

with a similar expression for m_2.

The translational fluctuation effect of interacting dipole first treated by Kirkwood (1936) is obtained by setting $E_1 = E_2 = E_0 e$. The first order reaction field term in eq. (8) vanishes on averaging over orientations with respect to the space-fixed field direction e, and the second term gives

$$B_{\varepsilon(in)} = \frac{32\pi^2 N^2 \alpha^3}{3}\int_0^\infty r^6 \exp(-\phi_{12}/kT) r^2 dr. \quad \ldots (9)$$

For the evaluation of $B_{\varepsilon(or)}$ we follow the method of perturbation expansion (the anisotropic interactions are treated as perturbation of central potential) and get

$$B_{\varepsilon(or)} = \frac{16\pi^2 N^2}{9kT}\sum_{p=0}^{\infty}\int_0^\infty\int_{\omega_1}\int_{\omega_2}\frac{(m_1+m_2)^2}{2p!}\left(\frac{V_{12}}{kT}\right)^p r^2 dr\, d\omega_1\, d\omega_2. \quad \ldots (10)$$

For $(m_1+m_2)^2$ we take the relation (Bose & Cole 1970)

$$(m_1+m_2)^2 = \frac{\alpha^2(\omega)^2}{r^8}[4\cos^2\theta_0+4\cos^2\theta_1+5\cos^4\theta_1+5\cos^4\theta_2-18\cos^2\theta_1\cos^2\theta_2$$
$$+8\sin\theta_1\cos\theta_1\sin\theta_2\cos\theta_2\cos\phi].$$

For convenience, we define the following reduced quantities

$$\begin{aligned} B^* &= B/b; \quad B_\varepsilon^* = B_\varepsilon/b^2 \\ C^* &= C/b^2; \quad b = \tfrac{2}{3}\pi N\sigma^3 \\ \alpha^* &= \alpha/\sigma^3; \quad T^* = kT/\varepsilon \\ t &= 2(\varepsilon/kT)^{\frac{1}{2}}; \quad \Theta^{*2} = \Theta^2/\varepsilon\sigma^5 \end{aligned} \quad \ldots (11)$$

where the symbols have their usual meanings.

In terms of these reduced quantities the dielectric second virial coefficient for the potential model of eq. (1) can be written as an infinite series in the form

$$\begin{aligned} B_\varepsilon^* = {} & B^*_{\varepsilon(in)}+B^*_{\varepsilon(or)}(12-6)+B_\varepsilon^*{}_{(or)}(\text{quad})+B^*_{(or)}(\text{anis}) \\ & +B^*_{(or)}(\text{quad-in dip})+B^*_{\varepsilon(or)}(\text{sh})+B^*_{\varepsilon(or)}(\text{quad}\times\text{anis}) \\ & +B^*_{\varepsilon(or)}(\text{quad}\times\text{sh})+B^*_{\varepsilon(or)}(\text{anis}\times\text{sh})+\ldots \end{aligned} \quad \ldots (12)$$

where

$$B^*_{\varepsilon(in)} = 2\alpha^{*3}t^{-1}H_6(t) \quad \ldots (12.1)$$

$$B^*_{\varepsilon(or)}(12-6) = \tfrac{1}{4}(\alpha^*\Theta^*)^2 t^{-2}(1+\tfrac{4}{5}K^2)\,H_8(t) \quad \ldots (12.2)$$

$$B^*_{\varepsilon(or)}(\text{quad}) = \frac{1}{40}\alpha^{*2}\Theta^{*4}\left[H_{12}(t)+\frac{405}{392}(\Theta^* t)^2 H_{18}(t)+\ldots\right] \quad \ldots (12.3)$$

$$B^*_{\varepsilon(or)}(\text{anis}) = \frac{2}{35}(\alpha^*\Theta^*)^2K(1-2{\cdot}275K)H_{14}(t)+\ldots \quad \ldots (12.4)$$

$$B^*_{(or)}(\text{quad-in dip}) = \frac{123}{560}\alpha^{*3}\Theta^{*4}[H_{16}(t)+0{\cdot}549\alpha^*(\Theta^*t)^2H_{21}(t)+\ldots] \quad \ldots (12.5)$$

$$B^*_{\varepsilon(or)}(\text{sh}) = \frac{4}{35}(\alpha^*\Theta^*)^2D[-H_{20}(t)+1{\cdot}2t^2DH_{32}(t)+\ldots] \quad \ldots (12.6)$$

$$B^*_{\varepsilon(or)}(\text{quad}\times\text{anis}) = \frac{47}{11200}(\alpha^*\Theta^{*2}t)^2KH_{19}(t)+\ldots \quad \ldots (12.7)$$

$$B^*_{\varepsilon(or)}(\text{quad}\times\text{sh}) = -\left(\frac{3}{560}\right)(\alpha^*\Theta^{*2}t)^2DH_{25}(t)+\ldots \quad \ldots (12.8)$$

$$B^*_{\varepsilon(or)}(\text{anis}\times\text{sh}) \quad -\frac{24}{175}(\alpha^*\Theta^*t)^2DKH_{26}(t)- \quad \ldots (12.9)$$

The function $H_n(t)$ are defined and tabulated by Buckingham & Pople (1955). For calculation we have chosen such molecules (e.g., N_2, CO_2 and C_2H_4) for which experimental data at many temperatures are available. For the potential parameters reported in *I* which represent successfully the viscosity and second virial coefficients data, first we have calculated the dielectric second virial coefficient of N_2, CO_2 and C_2H_4. From the calculation, we found that it is not possible to represent the experimental B_ε data with these parameters. Using the same set of σ and ε/k as obtained in *I* and given in table 1, we have next estimated the values of Θ and D to give the best fit with the pressure as well as dielectric second virial coefficients data. These values of Θ and D are recorded in table 2 together with the values of other parameters used in the calculation In table 2 we have also summarized the values of quadrupole moments as recommended by Stogryn & Stogryn (1966) and obtained from other sources. Table 3 compares the calculated and experimental values of second virial coefficient. It can be seen that the agreement between the calculated and experimental values is satisfactory over the entire temperature range of our interest. For all the three systems calculated values of the dielectric second virial coefficient of N_2, CO_2 and C_2H_4 are compared, respectively, with values obtained from experimental data in tables 4–6.

Table 1. Potential parameters derived form viscosity data (Das Gupta *et al* 1973)

Gas	σ(A)	ε/k (°K)
N_2	3·650	90·5
CO_2	4·065	171·9
C_2H_4	4·236	193·5

Table 2. Molecular quadrupole moment, shape and other parameters for second virial coefficient calculation

Gas	$\alpha(A)^3$	K	D	$\Theta \times (10^{26}$ e.s.u. cm^2) This	Stogryn & Stogryn (1966) recommended value	Other work: value	method	ref.
N_2	1·730	0·176	0·20	−1·52	−1·52	−1·40 ± 0·1	Induced birefringence	*a*
						1·50	Pressure induced absorption.	*b*
						1·64	Pressure induced infrared absorption (H_2).	*c*
						1·70	Nuclear spin relaxation (H_2).	*d*
						1·40	Microwave line broadening (SO_2).	*e*
						1·40	Rotation excitation cross section for N_2 by electrons.	*f*
						± 2·05	Second virial coefficient	*g*
						± 2·06	Second virial coefficient	*h*
						1·36	Quantal calculation	*g*
CO_2	2·925	0·257	0·20	+ 5·14	−4·30	−4·30 ± 0·2	Induced birefringence	*i*
						4·85	Nuclear spin relaxation (H_2).	*d*
						2·69	Microwaves line broadening (SO_2)	*e*
						5·90	Pressure-induded microwaves absorption.	*a*
						4·40	Foreign gas pressure-induced microwave absorption.	*i*
						5·00	Static dielectric constant	*j,k*
						± 4·10	Second virial coefficient	–
						± 3·00	Second virial coefficient	*h*
						−2·50	Quantal calculation	*m*
C_2H_4	4·269	0·158	0·21	±3·30	1·50	1·50	Induced birefringence	*i*
						1·30	Microwave line broadening (NH_3).	*n*
						2·60	Pressure induced microwave absorption.	*a*
						4·00	Static dielectric constant	*k*
						± 3·85	Second virial coefficient	–
						±3·45	Second virial coefficient	*h*

a. Birnbaum & Maryott (1962).
b. Ketelaar & Rettschnick (1963) Reddy & Cho (1965).
c. Van Kranendonk (1958).
d. Bloom *et al* (1965).
e Krishnaji & Chandra (1963).
f Engelhardt *et al* (1964).
g. Karplus & Kolker (1963).
h. Singh *et al* (1973).
i. Buckingham *et al* (1968).
j. Kielich (1965).
k. Johnston & Cole (1962).
l. Spurling & Mason (1967).
m. McClan (1963).
n. Gordy *et al* (1953). Smith (1956).

Table 3. Experimental and calculated values of pressure second virial coefficient

T(K)	$B(T)$ (cm³/mole)		T(K)	$B(T)$ (cm³/mole)	
	Calc.	Exptl.		Calc.	Exptl.
	N_2			CO_2	
277·6	−8·40	−8·50	262·6	−153·50	−159·89
311·6	−2·45	−2·73	309·6	−109·75	−111·30
348·2	3·40	3·31	353·1	−83·00	−80·90
398·2	8·98	9·05	423·2	−52·48	−46·30
477·2	15·28	15·40	473·2	−40·50	−36·70
523·1	18·24	18·24	523·2	−29·25	−25·10
623·1	23·45	23·41	573·2	−20·15	−16·30
748·1	24·89	24·73			
	C_2H_4				
263·1	−171·96	−172·80			
283·1	−149·43	−150·90			
313·1	−122·83	−123·00			
353·1	−95·95	−95·00			
373·1	−82·26	−83·20			
423·1	−62·00	−59·80			
473·1	−45·25	−42·90			

Ref. for experimental data :

N_2 : Holborn & Otto (1925); Michels *et al* (1934); Gunn (1958); Huff & Reed (1963); Witonsky & Miller (1963); Ku & Dodge (1967)

CO_2 : Michels & Michels (1935); MacCormack & Schneider (1950, 1951); Butcher & Dadson (1964); Masalov (1966). Dadson *et al* (1967)

C_2H_4 : Michels & Goldermans (1942); Bottomley *et al* (1950); Butcher & Dadson (1964); Thomas & Zander (1966).

Table 4. Experimental and calculated values of dielectric second virial coefficient B_ε (in cm⁶/mole²) for N_2

T(K)	$B_{(du)}$	$B_{(or)}$12–6)	$B_{(or)}$(q)	$B_{(or)}$(an)	$B_{(or)}$(q–ql)	$B_{(or)}$(sh)
242	1·927	1·976	0·079	0·019	0·045	−0·162
296	1·885	1·595	0·060	0·001	0·019	−0·116
306	1·885	1·595	0·045	0·010	0·015	−0·113
322	1·586	1·435	0·037	0·009	0·013	−0·109
344	1·516	1·362	0·034	0·007	0·111	−0·098

	$B_{(or)}$(q×an)	$B_{(or)}$(q×sh)	$B_{(or)}$(an×sh)	$B_{(or)}$	B (Calc.)	B (exptl.)	Ref
242	0·008	−0·004	−0·002	1·959	3·886	4·2(1·0)	*a*
296	0·006	−0·003	−0·002	1·570	3·455	2·0(1·0)	*a*
306	0·003	−0·002	−0·001	1·507	3·152	1·8(1·0)	*a*
322	0·001	−0·001	–	1·385	2·971	2·4	*b*
						1·0(1·0)	*a*
						0·6(0·2)	*c*
344	—	—	—	1·316	2·832	0·0(0·8)	–
						1·5(2·5)	*b*

a. Johnston *et al* (1964). *b*. Maryott & Buckley (1953). *c*. Orcutt & Cole (1967).

Table 5. Experimental and calculated values of dielectric second virial coefficient B_ε (in cm^6/mole) for CO_2

T(K)	$B_{(in)}$	$B_{(or)}$(12-6)	$B_{(or)}$(q)	$B_{(or)}$(an)	$B_{(or)}$(q–id)	$B_{(or)}$(sh)
302·4	7·709	33·808	13·950	1·007	1·515	−1·256
322·7	7·644	29·970	11·383	0·889	1·342	−1·153
348·0	7·486	27·371	9·474	0·763	1·134	−1·017

	$B_{(or)}$(q–an)	$B_{(or)}$(q–sh)	$B_{(or)}$(an×sh)	$B_{(or)}$	B (calc.)	B (exptl.)	Ref
302·1	0·348	0·331	2·185	46·856	54·565	57·6(0·9)	*a*
322·7	0·291	−0·283	−1·873	40·566	48·210	50·7(0·93)	*a*
						41·4(2·4)	*b*
						49·7	*c*
348·0	0·232	−0·233	−1·533	36·191	43·677	46·4	–

c. Buckingham *et al* (1968).

Table 6. Experimental and calculated values of dielectric second virial coefficient B_ε (in cm^6/mole^2) for C_2H_4

T(K)	$B_{(in)}$	$B_{(or)}$(12-6)	$B_{(or)}$(q)	$B_{(or)}$(an)	$B_{(or)}$(q–id)	$B_{(or)}$(sh)
298·0	20·898	27·719	0·181	0·802	0·643	−1·026
301·7	20·374	24·117	0·168	0·724	0·402	−0·928
323·0	20·199	22·332	0·151	0·683	0·397	−0·859
373·0	19·519	21·646	0·122	0·551	0·349	−0·735
423·0	19·078	16·660	0·098	0·438	0·285	−0·635

	$B_{(or)}$(q–an)	$B_{(or)}$(q–sh)	$B_{(or)}$(an×sh)	$B_{(or)}$	B (calc.)	B (exptl.)	Ref
298·0	0·048	−0·091	−1·224	26·882	47·780	31·5	*a*
304·7	0·054	−0·084	1·185	23·598	43·972	14·3	*a*
323·0	0·047	−0·075	−0·999	21·677	41·876	47·5(1·4)	*b*
						49·9(2·0)	*b*
373·0	0·038	0·061	−0·864	21·046	40·565	42·2(2·8)	*b*
						41·4(1·2)	*b*
423·0	0·029	−0·049	−0·643	16·178	35·256	37·6(2·4)	*b*

a. Buckingham *et al* (1968). *b*. Bose & Cole (1971).

(b) *Third virial coefficient*

For the calculation of third virial coefficient we have adopted the procedure outlined by Stogryn (1969, 1970). In this perturbation expansion method tensor forces are treated as perturbation of central forces. For the third virial coefficient the perturbation series can be written as

$$C^*(T^*) = C^{*(0)}(T^*) + C^{*(1,a)}(T^*) + C^{*(2,a)}(T^*) + C^{*(3,a)}(T^*) + \ldots$$

$$+ C^{*(1,non)}(T^*) + C^{*(2,non)}(T^*) + \ldots \qquad \ldots (13)$$

In this equation the number in superscript indicates the order of perturbation and letters *a* and *non*, respectively, the contributions arising from pair and three-body nonadditive interactions.

The zero order perturbation term $C^{*(0)}(T^*)$ is the reduced third virial coefficient of a Lennard-Jones (12-6) system and is given as

$$C^{*(0)}(T^*) = T^{*-1/2} \sum_{n=0}^{\infty} C_n(0) T^{*-n/2}. \qquad \ldots (14)$$

In the first order of perturbation we find that only the induction interaction of pair potential and the dispersion and repulsion of triplet potential contribute and the contributions of other brncahes are zero. Thus

$$C^{*(1,a)}(T^*) = C^{*(11,a)}(\text{in})$$

and $\qquad \ldots (15)$

$$C^{*(1,non)}(T^*) = C^{*(1,non)}(\text{dis}) + C^{*(1,non)}(\text{rep})$$

where

$$C^{*(1,a)}(\text{in}) = 9\alpha^{*}\Theta^{*2} T^{*-5/6} \sum_{n=0} C_n(8) T^{*-n/2} \qquad \ldots (15.1)$$

$$C^{*(1,non)}(\text{dis}) = \alpha^{*} T^{*-3/4} \sum_{n=0}^{\infty} C_n^{non}(0) T^{*-n/2} \qquad \ldots (15.2)$$

$$C^{*(1,non)}(\text{rep}) = \frac{6}{T^*} \int_0^{\infty} \int_{1/2}^{1} \int_{1-y}^{y} \exp\left[-\sum_{i,j=1}^{3} \phi^{*}(i,j)/T^* \right]$$

$$\times (xy)^{-6} R^{*-16} [y^{-6} \cos 20_x + x^{-6} \cos 20_y + (xy)^{-6} \cos 20] dx dy dR^* \qquad \ldots (15.3)$$

In the second order of perturbation, the contribution to the third virial coefficient arises from the squares of permanent moment, induction, dispersion and overlap terms as well as cross terms such as products of permanent moment and induced moment etc. of pair potential. We shall, however, drop all terms which contain $V^{in}{}_{ij}$ and $V^{in}{}_{ijk}$ with powers greater than one from $C^{*(2,a)}$ and $C^{*(2,non)}$ because the expressions for $V^{in}{}_{ij}$ and $V^{in}{}_{ijk}$ are correct to only first power in the polarizability. Thus

$$\begin{aligned} C^{*(2,a)} = {} & C^{*(2,a)}(\text{quad}) + C^{*(2,a)}(\text{dis}) + C^{*(2,a)}(\text{sh}) + C^{*(2,a)}(\text{quad} \times \text{in}) \\ & + C^{*(2,a)}(\text{quad} \times \text{dis}) + C^{*(2,a)}(\text{in} \times \text{sh}) + C^{*(2,a)}(\text{dis} \times \text{sh}) \\ & + C^{*(2,a)}(\text{dis} \times \text{dis}) \end{aligned} \qquad \ldots (16)$$

and

$$C^{*(2,non)} = C^{*(2,non)}(\text{quad}\times\text{in}) + C^{*(2,non)}(\text{dis}\times\text{in}) + C^{*(2,non)}(\text{dis}) + C^{*(2,non)}(\text{quad}\times\text{dis}) + C^{*(2,non)}(\text{dis}\times\text{dis}) \quad \ldots (17)$$

where

$$C^{*(2,a)}(\text{quad}) = \frac{21}{5}\Theta^{*4}T^{*-5/3}\sum_{n=0}^{\infty} C_n(10)T^{*-n/2} \quad \ldots (16.2)$$

$$C^{*(2,a)}(\text{dis}) = \frac{24}{5}K^2(2+3{\cdot}8K^2)T^{*-3/2}\sum_{n=0}^{\infty} C_n(12)T^{*-n/2} \quad \ldots (16.2)$$

$$C^{*(2,a)}(\text{sh}) = \frac{192}{5}D^2T^{*-1/2}\sum_{n=0}^{\infty} C_n(24)T^{*-n/2} \quad \ldots (16.3)$$

$$C^{*(2,a)}(\text{quad}\times\text{in}) = -\frac{216}{35}\alpha^*K\Theta^{*14}T^{*-17/12}\sum_{n=0}^{\infty} C_n(13)T^{*-n/2} \quad \ldots (16.4)$$

$$C^{*(2,a)}(\text{quad}\times\text{dis}) = \frac{432}{25}K^2\Theta^{*2}T^{*-19/12}\sum_{n=0}^{\infty} C_n(11)T^{*-n/2} \quad \ldots (16.5)$$

$$C^{*(2,a)}(\text{in}\times\text{sh}) = -\frac{576}{35}\alpha^*\Theta^{*2}DT^{*-5/6}\sum_{n=0}^{\infty} C_n(20)T^{*-n/2} \quad \ldots (16.6)$$

$$C^{*(2,a)}(\text{dis}\times\text{sh}) = -\frac{192}{5}KDT^{*-1}\sum_{n=0}^{\infty} C_n(18)T^{*-n/2} \quad \ldots (16.7)$$

$$C^{*(2,a)}(\text{dis}\times\text{dis}) = \frac{48}{5}K^2T^{*-3/2}\sum_{n=0}^{\infty} \bar{C}_n(12)T^{*-n/2} \quad \ldots (16.8)$$

$$C^{*(2,non)}(\text{quad}\times\text{in}) = -\frac{9}{20}\alpha^*\Theta^{*4}T^{*-17/12}\sum_{n=0}^{\infty} \bar{C}_n(13)T^{*-n/2} \quad \ldots (17.1)$$

$$C^{*(2,non)}(\text{dis}\times\text{in}) = \frac{18}{25}\alpha^*K^2\Theta^{*2}T^{*-4/3}\sum_{n=0}^{\infty} C_n(14)T^{*-n/2} \quad \ldots (17.2)$$

$$C^{*(2,non)}(\text{dis}) = \frac{9}{2}\alpha^{*2}T^{*-1}\sum_{n=0}^{\infty} C'_n(18)T^{*n/2} \quad \ldots (17.3)$$

$$C^{*(2,non)}(\text{quad}\times\text{dis}) = \frac{324}{25}\alpha^*K^2\Theta^{*2}T^{*-4/3}\sum_{n=0}^{\infty} C'_n(14)T^{*-n/2} \quad \ldots (17.4)$$

$$C^{*(2,non)}(\text{dis}\times\text{dis}) = \frac{36}{25}\alpha^*K^2(10+19K^2)T^{*-5/4}\sum_{n=0}^{\infty} C'_n(15)T^{*-n/2} + \frac{144}{25}\alpha^*K^2(10-K^2)T^{*-5/4}\sum_{n=0}^{\infty} C'_n(15)T^{*-n/2}. \quad \ldots (17.5)$$

For all the systems studied in this paper we find that a proper convergence of perturbation series for all branches of pair and triplet potentials except quadrupole-quadrupole interaction branch of pair potential is achieved through the second order term. In the calculation of the third-porder perturbation term we therefore consider only the quadrupole interaction and neglect all other branches of the potential. Thus

$$C^{*(3)} = C^{*(3,a)}(\text{quad}) + C^{*(3,a)}(\text{quad} \times \text{quad}) \quad \ldots (18)$$

where

$$C^{*(3,a)}(\text{quad}) = -\frac{216}{245}\Theta^{*6}T^{*-9/4}\sum_{n=0}^{\infty} C_n(15)T^{*-n/2} \quad \ldots (18.1)$$

$$C^{*(3,a)}(\text{quad} \times \text{quad}) = -\frac{3}{200}\Theta^{*6}T^{*-9/4}\sum_{n=0}^{\infty} \bar{C}_n(15)T^{*-n/2}. \quad \ldots (18.2)$$

The expression coefficients $C_n(u)$, $C_n(u)$, $C'_n(u)$ and $C'_n(u)$ which appear in above equations are triplet integrals over positions and orientations of three particles forming a triangle. These functions are tabulated by Stogryn (1968, 1969, 1970) for many values of n and u.

For the potentials parameters found suitable in sec. 2a to represent viscosity, second and dielectric second virial coefficients, we have calculated the additive and non-additive contributions to the third virial coefficient for N_2, CO_2 and C_2H_4 for many values of T^*. From the calculation we find that at low temperatures all branches of pair and triplet interactions contribute substantially to the third virial coefficient. However, at high temperatures $C^{(1,a)}(\text{in})$, $C^{(2,non)}(\text{in})$, and $C^{(2,non)}(\text{dis})$ are small. The induction and dispersion nonadditive contributions are always positive corresponding to the three body nonadditive energy being repulsive for most of the orientations, and fall off with increasing temperature as induction and dispersion forces become less important. The repulsive nonadditive contribution is always negative, corresponding to the repulsion three-body interaction being attractive for most orientations. The $C^{(1,non)}(\text{rep})$ and $C^{(1,non)}(\text{dis})$ are substantial at all temperatures. The overall effect of the nonadditive contribution to the third virial coefficient is that it shifts the maximum in additive contribution to somewhat lower temperature and increase the value of maximum.

For N_2 and C_2H_4 we find that the proper convergence is achieved through the third order perturbation term. For CO_2 the higher order terms in the additive contribution arising from the quadrupole interaction is, however, not negligible. In fact, $C^{(3,a)}$ (quad) is small and opposite to $C^{(2,a)}(\text{quad})$ at all temperatures. We therefore, use the following simple [1, 0] Pade' approximation to evaluate the total contribution due to quadrupole interaction.

$$C^{(a)}(\text{quad}) = C^{(2,a)}(\text{quad})\left[1 - \left|\frac{C^{(2,a)}(\text{quad})}{C^{(3,a)}(\text{quad})}\right|\right]^{-1}. \quad \ldots (19)$$

Recently Verlet & Weiss (1974) have shown that the above Pade' approximation gives excellent result for a series which fulfil the condition given above.

3. Discussion

It can be seen from the table 2 that the values of Θ_{N_2} obtained here is same as recommended by Stogryn & Stogryn (1966) and is in excellent agreement with the value obtained from induced birefringence study (Buckingham *et al* 1968). $\Theta_{C_2H_4}$ is closed to the value obtained in *I*. For CO_2 we get a larger value of Θ than the reported in *I*. The pressure induced microwave absorption study by Birnbaum & Maryott (1962) and nuclear spin relaxation study by Bloom *et al* (1965) lead, respectively, to a value of $\Theta_{CO_2} = 5{\cdot}9\times10^{-26}$ e.s.u. cm^2 and $4{\cdot}8\times10^{-26}$ e.s.u. cm^2. A static dielectric constant calculation (Kielich 1965, Johnston & Cole 1962) leads to a value of $\Theta_{CO_2} = 5{\cdot}0\times10^{-26}$ e.s.u. cm^2. Our value of Θ_{CO_2} is close to these values.

Regarding the shape parameter D as has already been mentioned elsewhere (Pople 1954) a negative D corresponds to a plate like molecule and a positive D to a rod like one. If we compare the ratio of a length l to width d as calculated from the known molecular geometries and the Van der Waals radii of the peripheral atoms, we find that l/d for H_2 and CO_2 is almost the same, ($l/d = 2{\cdot}6$). Singh & Datta (1970) by a similar analysis zas presented here have obtained D for Deuterium molecule as 0·22 which is in good agreement with the theoretically calculated values of Boer (1942), and Roberts (1963). On the basis of above argument we expect that D for CO_2 should be near 0·22. Our value $D_{CO_2} = 0{\cdot}20$ is in good agreement with this expectation. Same value of D for CO_2 has been obtained by Datta & Singh (1971) using Kihara model for central potential. Our values of D_{N_2} and $D_{C_2H_4}$ are expected to be realistic and show that molecules are rod like.

It can be seen from the tables 4–6 that for all the three systems N_2, CO_2 and C_2H_4 we have obtained a substantially better agreement between calculated and experimental dielectric second virial coefficients, than in previous work. The experimental values of B are scanty and at the same time not very precise. Moreover, the values reported by different authors differ from each other considerably. In view of these uncertainties the agreement found by us is satisfactory.

Figures 1–3 compare the calculated and experimental third virial coefficients of N_2, CO_2 and C_2H_4. For all the three systems we get a reasonably good agreement between theory and experiment. As the experimental values of the third virial coefficients are derived from gas compressibility measurements by fitting an isotherm with a polynomial in the density, the values are subject to uncertainties, in the isotherm and the degree of polynomial used, in addition to

the experimental inaccuracies. Owing to these reasons the agreement found here is satisfactory.

In figures 1 and 2, the values given by dashed line are those as calculated by Stogryn (1970). This calculation differs from that of ours in the following sense :

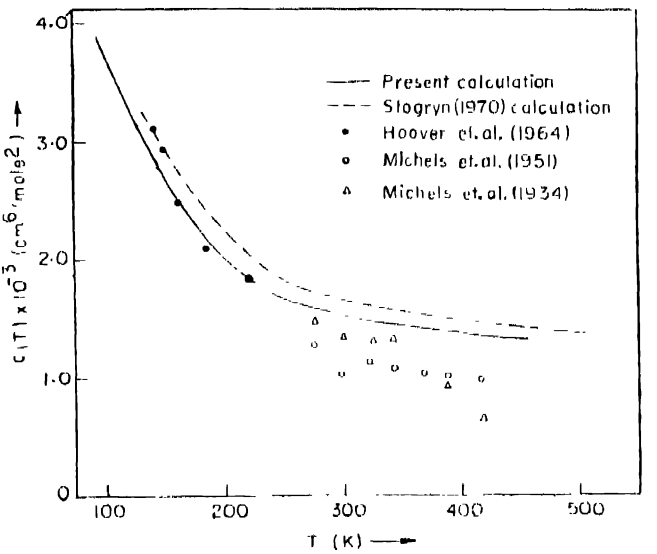

Fig. 1 Comparison of calculated and experimental third virial coefficients for N_2

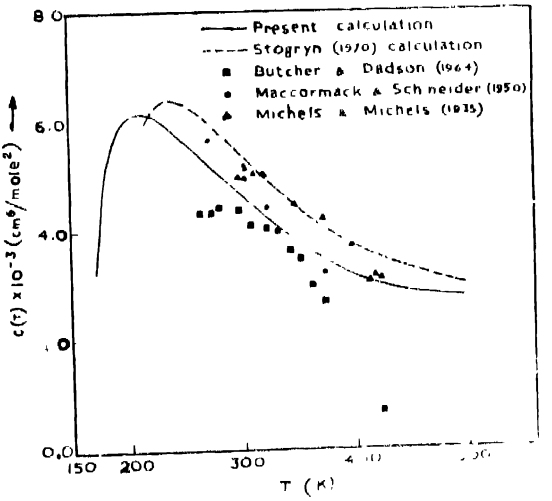

Fig. 2. Comparison of calculated and experimental third virial coefficients for CO_2.

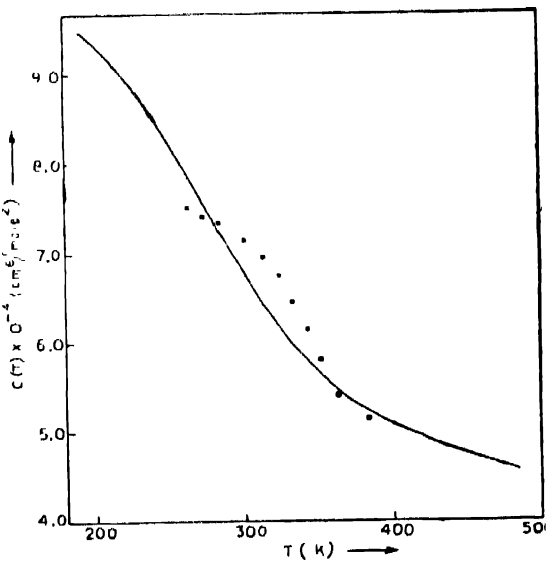

Fig. 3. Comparison of calculated and experimental third virial coefficients for C_2H_4 : calculated (–) curve and experimental points (Butcher & Dadson 1964).

1. The values of central force parameters σ and ϵ/k determined by Spurling & Mason (1967) from viscosity data on 12-6-5 potential model has been used by Stogryn. The value of Θ which he has taken do not explain the viscosity and the second virial coefficients. Thus the parameters used by Stogryn cannot explain all the three properties.

2. The pair anisotropic overlap and repulsion three-body nonadditive interaction which contribute substantially to the third virial coefficient has been neglected by Stogryn.

In conclusion, we can summarize that by making use of the concept that the transport coefficients are less sensitive to the angle-dependent parts of the interaction than the virial coefficients, we have been able to represent the viscosity, dielectric second, pressure second and third virial coefficients of nonpolar polyatomic molecules with the same set of force parameters.

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